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Alkyl chain length effects on solid-state difluoroboron β-diketonate mechanochromic luminescence[†]

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Solid-state difluoroboron β -diketonate dyes display reversible mechanochromic luminescence (ML). To test the effects of alkyl chain length on solid state photoluminescence and ML, a series of dyes, BF₂dbmOR, with dibenzoylmethane (dbm) ligands and alkoxyl substituents (–OR) were prepared, where R = C_nH_{2n+1} and n = 1, 2, 3, 5, 6, 12, 14, 16, 18. Emission properties were investigated in solution and in the solid state. Fluorescence spectra and lifetimes were nearly identical for dyes in CH₂Cl₂ solution; whereas, in the solid state, as powders, thin films or spin cast films, emission maxima, and lifetimes were different among the samples. Solid-state ML emission spectra were monitored at room temperature as a function of time for smeared powders on quartz surfaces. The recovery time generally increased with alkyl chain length, ranging from minutes (n = 3) to days (n = 18). Longer chain analogues (n = 6, 12, 14, 16, 18) did not fully return to the original annealed emissive state even after months on quartz, though the dynamics are substrate dependent. Solid-state dyes were also investigated by XRD and DSC (powders), and by AFM (spin cast films).

Introduction

Mechanochromic luminescence (ML) refers to the phenomenon whereby luminescent materials change their emission colors in response to mechanical stimuli such as grinding, smearing, and pressing.1 Such phenomena have been observed with liquid-crystalline²⁻⁴ and crystalline solids,⁵⁻¹² as well as dye-doped polymers.¹³⁻¹⁶ The causative mechanisms have been attributed to mechanically induced structural changes in the solid-state molecular assemblies. For example, Sagara *et al.* reported that a liquidcrystal pyrene derivative has yellow emission in the cubic phase, but switches to blue shifted emission upon mechanically induced columnar phase formation, creating different hydrogen bonding patterns and $\pi - \pi$ stacking interactions.³ More commonly, mechanical switching between ordered and amorphous states results in changes in optical properties.^{5,9} In another study, alkyl substituent effects on cyano-substituted oligo(p-phenylene vinylene) derivatives (cyano-OPVs) were noted. Cyano OPVs with C12 and C18 alkoxyl substituents possessed ML but a methoxy analogue did not.6 Even though mechanisms for ML have been proposed and compelling evidence has been shown in some cases,

in-depth, predictive understanding of this phenomenon is still limited. Further study of the relationship between molecular structure and mechanochromic behavior is merited.¹

Difluoroboron diketonates (BF₂bdks) are classic dyes possessing impressive luminescent properties such as large extinction coefficients,¹⁷⁻¹⁹ two-photon absorption cross-sections,²⁰ high fluorescence quantum yields,¹⁷⁻¹⁹ and unusual room-temperature phosphorescence²¹ (RTP) in solid-state media (*e.g.* polymers). Due to these many interesting properties, difluoroboron diketonate derivatives have been exploited as tumor hypoxia imaging agents,²² anion receptors,²³ and NIR probes for amyloid- β deposits in Alzheimer's disease.²⁴ In addition, the solid-state photophysical properties of BF₂bdks have been studied by Mirochnik *et al.*,²⁵ who have shown that these dyes display size-dependent luminescent and thermochromic properties.

Recently, we discovered that BF_2AVB (AVB = avobenzone) possesses polymorphism and reversible mechanochromic luminescence. BF_2AVB crystals possess different emission colors depending on the crystal types and processing conditions: blue (dendritic), cyan (needle) and green (prism). When crystals are crushed and solid samples are smeared, the emission color shifts significantly to yellow-orange. Surprisingly, smeared materials can spontaneously revert back to the original green-blue emission at room temperature, or alternatively, the process may be facilitated by thermally annealing (TA).²⁶ Similar observations have been noted for $BF_2dbmOC_{12}H_{25}$ (C12) analogues.^{27,28} Smearing the C12 powder on weighing paper red-shifted the emission color of the dyes, but upon thermally annealing, the emission color significantly blue-shifted.²⁷ Interestingly, a similar dye, $BF_2dbmOCH_3$ (C1), does not possess mechanochromism;

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the emission spectra stayed the same upon smearing or thermally annealing. Notably, the structures of BF₂AVB, BF₂dbmOC₁₂H₂₅, and BF₂dbmOCH₃ only differ in the alkyl substituent: tert-butyl, C12 alkyl chain and a methyl group. These observations inspired us to conduct a systematic study of the effects of the alkyl chain length on the solid state optical properties and mechanochromic behavior of BF2dbm. In this account, a series of BF₂dbmOR derivatives (where $R = C_n H_{2n+1}$ and n = 1, 2, 3, 5, 6, 12, 14, 16, 18) were synthesized and the luminescent properties in the solution and solid-state (powders, thin films and spin cast films) were studied by fluorescence spectroscopy and lifetime measurements. (Note: C1 and C12 were prepared and investigated again here for reference.) We also investigate the solid-state luminescence and ML phenomenon via XRD and AFM. For simplicity, we will refer to these dyes as **C***n*, where *n* is the number of carbon units on the alkoxyl chain.



Experimental

Materials

Solvents CH_2Cl_2 and THF were dried and purified by passage through alumina columns. 4-Ethoxyacetophenone, $BF_3 \cdot Et_2O$ (purified, redistilled), and all other chemicals were reagent grade from Sigma-Aldrich and were used as received without further purification. Synthesis and characterization data for **C1–C18** are provided in the ESI[†].

Methods

¹H NMR (300 MHz) spectra were recorded on a UnityInova 300/ 51 instrument in CDCl₃ unless indicated otherwise. ¹H NMR spectra were referenced to the signal for chloroform residual proton at 7.26 ppm and coupling constants are given in Hertz. Melting and crystallization temperatures, $T_{\rm m}$ and $T_{\rm c}$, were recorded on a TA Instruments Modulated DSC 2920 (scanning rate 5 °C min⁻¹). A Laurel Technologies WS-650S spin-coater was used to cast **Cn** (*n* = 1, 2, 3, 5, 6, 12, 14, 16, 18) films at 3000 rpm for steady-state luminescence spectroscopy and AFM studies. The films were fabricated by preparing 1 mg mL⁻¹ solutions of Cn in CH₂Cl₂, followed by adding 10–11 drops of the solution onto a circular microscope cover glass (d = 25 mm). The spin cast films were then dried in vacuo for an additional ~15 to 30 min before measurement. Photographs were taken with a Canon PowerShot SD780 IS Digital ELPH. UV/vis spectra were recorded on a Hewlett-Packard 8452A diode-array spectrophotometer. Steady-state fluorescence emission spectra were recorded on a Horiba Fluorolog-3 Model FL3-22 spectrofluorometer (double-grating excitation and double-grating emission

monochromator). Time-correlated single-photon counting (TCSPC) fluorescence lifetime measurements were performed with a NanoLED-370 ($\lambda_{ex} = 369$ nm) excitation source and a DataStation Hub as the SPC controller. Lifetime data were analyzed with DataStation v2.4 software from Horiba Jobin Yvon. Fluorescence quantum yields, $\Phi_{\rm F}$, in CH₂Cl₂ were calculated versus anthracene in EtOH as a standard as previously described²⁹ using the following values: $\Phi_{\rm F}$ anthracene = 0.27,³⁰ $n_{\rm D}^{20}$ EtOH = 1.360, $n_{\rm D}^{20}$ CH₂Cl₂ = 1.424. Optically dilute CH₂Cl₂ solutions of Cn and the EtOH solution of the anthracene standard were prepared in 1 cm path length quartz cuvettes with absorbances <0.1 (a.u.). For ML recovery time measurements, solid-state fluorescence spectra ($\lambda_{ex} = 365$ nm) were recorded on a Horiba Fluorolog-3 Model FL3-22 spectrofluorometer equipped with a Tiffen 58 mm neutral density 0.6 filter to maximize the surface area while preventing photobleaching. The dyes (\sim 3 mg) were rubbed onto the outside surface of a quartz cuvette with a cotton swab tip, and were thermally annealed in an oven at 110 $^{\circ}$ C for 5 min. After cooling for ~5 min, emission spectra were recorded, the thin dye layers were smeared with a fresh cotton swab tip, and emission spectra were recorded as a function of time. X-Ray diffraction (XRD) (Smart-Lab, Rigaku Inc.) (Cu K_{α} source, 0.154 nm) was used to determine the crystallinity of annealed and smeared samples and all the measurements were performed at room temperature. The sample morphologies for spin-cast films were characterized by Atomic Force Microscopy (AFM) (Digital Image, DI 3000) in tapping mode. The scan area was 20 μ m \times 20 μ m with a scan rate of 0.8 Hz.

Results and discussions

Synthesis and solution optical properties

BF2dbmOR were synthesized via standard Claisen condensation of the appropriate alkoxyacetophenone with methyl benzoate, followed by boronation in CH₂Cl₂, purification by column chromatography and recrystallization with 1:1 CH₂Cl₂/ hexanes. All the boron dyes were obtained as yellow powders with solid-state emission colors ranging from yellow to cyan upon UV excitation ($\lambda_{ex} = 365 \text{ nm}$) (Fig. 1a). In CH₂Cl₂ solution, all the samples displayed absorption maxima at 399 ± 1 nm and exhibited high extinction coefficients, ranging from 50 100 to 66 200 (M⁻¹ cm⁻¹), similar to related boron diketonate dyes.^{17,18,21} They showed emission maxima at $435 \pm 1 \text{ nm}$ (fwhm \approx 52 nm), high quantum yields ($\Phi_{\rm F} > 0.82$), and similar fluorescence lifetimes (~ 2.0 ns) that were fitted to single exponential decay (Fig. S1 and Table S1[†]). In summary, all these dyes behaved similarly, thus indicating that increasing the alkyl chain length on the alkoxyl group did not substantially affect the photophysical properties in solution.

Solid-state optical properties

Powders. In contrast to the solution properties, the solid-state photoluminescent properties varied significantly when altering the alkoxyl chain length. First, emission properties of powders obtained from synthesis after recrystallization from 1:1 CH₂Cl₂/hexanes were investigated. Fluorescence spectra and lifetimes are shown in Fig. 1c and Table 1 respectively. The dye series showed a trend from yellow to cyan with increasing alkyl



Fig. 1 Images of (a) powders obtained from recrystallization and (b) thin films formed by slow evaporation (SE) of 2 mg mL⁻¹ solution of Cn in CH₂Cl₂. Normalized emission spectra for powders are shown in (c) and for thin films in (d) ($\lambda_{ex} = 365$ nm).

chain length; however, at C12, samples appeared to reach a threshold, given that emission maxima of \sim 473 nm were observed for C12–C18, even as the alkoxyl chain length increased. For C1, the long lifetime (30.94 ns) and broad, structureless band have been attributed to excimer emission.³¹

 Table 1
 Fluorescence properties of solid-state Cn dyes

			Spin-cast films	
	Powder $\lambda_{\rm em}^{\ a}$ $(\tau_{\rm pw0}^{\ b})$	Thin films $\lambda_{\rm em}^{\ a}$ $(\tau_{\rm pw0}^{\ b})$	$\begin{array}{c} \mathrm{UA} \lambda_{\mathrm{em}}{}^{a} \\ (\tau_{\mathrm{pw0}}{}^{b}) \end{array}$	$ \begin{array}{c} {\rm TA} \; \lambda_{\rm em}{}^a \\ (\tau_{\rm pw0}{}^b) \end{array} $
C1	550 (30.94)	544 (35.91)	544 (44.35)	540 (40.85)
C2	507 (5.13)	473 (6.21)	499 (11.18)	497 (9.31)
C3	500 (4.22)	501 (4.72)	523 (31.56)	482 (6.31)
C5	496 (7.67)	491 (5.82)	511 (25.54)	453 (4.22)
C6	489 (6.21)	483 (6.33)	506 (14.58)	478 (5.40)
C12	473 (3.29)	474 (6.53)	504 (19.96)	466 (6.43)
C14	476 (3.90)	480 (4.63)	510 (26.68)	457 (4.95)
C16	471 (3.91)	475 (5.22)	507 (19.71)	470 (3.11)
C18	473 (3.05)	479 (2.18)	518 (30.56)	472 (3.48)
C16 C18 ^a Unit	471 (3.91) 473 (3.05)	475 (5.22) 479 (2.18)	507 (19.71) 518 (30.56) weighted lifetim	470 (3.11 472 (3.48

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However, for **C2–C18**, much shorter lifetimes were observed $(\tau_{pwo}{}^{32} = 3-7 \text{ ns})$, suggesting different dye emissive species. Light reabsorption or light scattering associated with the bulk powder,^{33–35} and aggregation effects (*e.g.* ground state structures)³⁶ may be contributing to these differences. This is supported by XRD studies for select powder samples that show evidence of crystallinity (Fig. 4, green lines), with **C6**, **C12**, and **C18** displaying very similar features (*i.e.* strongest peaks at ~25°, ~19°, and ~6° 2 θ), and a different diffraction pattern for the smaller **C2**, suggesting different crystal packing. The sample thickness and processing can also play a role. This has been seen previously for BF₂AVB, where different fabrication methods and associated solid-state morphologies give rise to different optical properties.²⁶ Thus, films fabricated by slow evaporation (SE) and spin-casting (SC) methods were also investigated for **C1–C18**.

Films by slow evaporation (SE). Films of C1-C18 were formed by slow evaporation of CH_2Cl_2 dye solutions (2 mg mL⁻¹) in small glass vials. Visual inspection through a magnifying glass revealed crystalline morphologies on the sides of the vials. The C1 SE film exhibited yellow emission, C2 and C12-C18, blue, and C3–C6, yellow-green upon UV excitation ($\lambda_{ex} = 365$ nm) (Fig. 1b). Spectral data are provided in Fig. 1d and Table 1. Previously Mirochnik showed that C1 crystals display excimer fluorescence,³¹ which is similar to C1 data here. With the exception of C2 which is considerably blue shifted relative to the powder, all other Cn SE films had nearly identical emission maxima to powder samples, with emission maxima blue shifting with increasing alkoxyl chain length. Typical for heterogeneous solid-state samples, lifetime measurements for C2-C18 show multiexponential decays, with pre-exponential weighted lifetimes $(\tau_{pw0})^{32}$ ranging from 2–6.5 ns. Again, a much longer lifetime was measured for C1 ($\tau_{pw0} = \sim 36$ ns), ascribed to excimer formation³¹ (Tables 1 and S2[†]). In summary, luminescence properties are similar for crystalline powders and SE films, with the exception of C2 which displays sensitivity to these fabrication conditions.

Spin-cast (SC) films. To obtain even thinner, more amorphous films, 1 mg mL⁻¹ CH₂Cl₂ dye solutions were spin-cast at 3000 rpm onto glass substrates. Images and steady-state fluorescence spectra for representative as-spun (*i.e.* unannealed (UA)) samples are shown in Fig. 2 and a full set of data is included in the ESI (Fig. S2†). All **CnUA** film spectra showed broad, featureless bands with red shifted emission ($\lambda_{em} \approx 510$ nm, except for C3, $\lambda_{em} = 523$ nm) and long lifetimes (τ_{pw0} range = 15–32 ns) that could be fitted to multiexponential decays. Like **C1** powders and SE films and previously reported spin cast boron bdk dyes,^{26,27} these observations point to excimeric species in the amorphous UA films.³⁷ Unannealed spin-cast film emission maxima for C3–C18UA did not follow the chain length dependent trend observed for crystalline powders and SE films. Here, C5UA and C14UA were the most blue-shifted analogues.

Because heating typically results in more ordered morphologies for this family of dyes,^{26–28,36} thermally annealed SC films were also investigated. Heating was conducted at 110 °C for 5 minutes (*i.e.* below the melting temperatures, T_m , for the dyes which range from 126–188 °C; Table S4†). A previous study showed that **C12** as-spun films (*i.e.* unannealed (UA)) displayed



Fig. 2 Images and steady state fluorescence spectra of unannealed (UA) and thermally annealed (TA) spin-cast films for (a) C2, (b) C3, (c) C5, (d) C6, (e) C12, and (f) C18. Thermally annealing = $110 \degree$ C for 5 min.

red shifted emission maxima compared to thermally annealed (TA) films.²⁷ The difference in spectral data from UA to TA has been ascribed to the transition from amorphous to ordered states after heat treatment. Similar results were also observed for other **Cn** dyes, with variations in spectral shift across the series.

The emission color and spectra of C1 and C2 did not change when as-spun films were thermally annealed; however, the band features were different among the two compounds. While C1 films displayed a broad, featureless band at ~544 nm ($\tau_{pw0} = ~44$ ns and close to single exponential), C2 films possessed narrower band emission with blue-shifted maxima (~497 nm) and much shorter lifetimes ($\tau_{pw0} = ~9$ ns) (Table 1, Fig. 2 and S2†). In contrast, for C3TA–C18TA, thermal annealing induced ~30 to 60 nm hypsochromic shifts and TA samples possessed shorter lifetimes ($\tau_{pw0} = ~3$ to 6 ns) that could also be fitted to double or triple exponentials. Although it is not clear why the C5 sample should be unique, it exhibited distinctive luminescence properties, namely, a very sharp peak at 453 nm (fwhm = 50 nm). Interestingly, this is similar to the strongly blue shifted, narrow bandwidth emission corresponding to one of the BF₂AVB crystal forms (*i.e.* dendritic, $\lambda_{em} = 459$ nm, fwhm = 31 nm) reported previously.²⁶ Coincidentally, these two compounds possess the same molecular weight.

The film morphologies before and after heating were explored by atomic force microscopy (AFM) for select samples with notable emission behavior: C2UA/TA showed no difference, C3UA displayed the most red-shifted maximum, C5TA was most blue-shifted with the sharpest peak compared to other dyes, and finally, C18 is the longest chain analogue, for comparison (Fig. 3). For C2, there is little change upon thermal treatment; the crystal size increased slightly and the shape remained similar throughout, consistent with C2UA/TA emission data. On the other hand, C3UA, C5UA and C18UA films all displayed largely



Fig. 3 AFM images of unannealed (left-UA) and thermally annealed (TA-right) spin-cast films of C2, C3, C5, and C18.

amorphous morphologies that became much more crystalline upon heating. **C3TA** crystals are equiaxed; whereas, **C5TA** and **C18TA** are more needle-like in habit. The crystal size generally increased with chain length for the samples explored. In summary, AFM data support the notion that differences in emission spectra between UA and TA spin-cast films are ascribed to the transition from more amorphous, disordered states to more ordered, crystalline states. This is similar to other difluoroboron diketonate dyes studied so far.^{26,27,36}

Because powders, slow evaporated and thermally annealed spin cast films all possess crystalline morphologies, it is interesting to compare their emission behavior, to gain insight into processing effects (Table 1). All TA films show blue shifted emission compared to bulk powders. The magnitude of the shift varies across the series, but with no obvious trend. For example, C5TA displayed the largest hypsochromic shift compared to the powder (\sim 43 nm), while C16 and C18 possessed the smallest changes (i.e. 1 and 2 nm, respectively). One possible explanation for these differences in bulk and thin samples is reabsorption and emission due to differences in sample thickness. However, that the differences are so small for some samples (e.g. C16, C18) regardless of thickness, argues against this. Alternatively, longer spacers may dilute the dyes and diminish dye-dye interactions. even in the bulk, however, this is not a consistent trend across the series (Table 1). What can be said with certainty is that some dyes show dramatically different properties with certain fabrication methods (e.g. C2 for SE films and C5 and C14 for thermally annealed spin cast films), and the most dramatic differences are between amorphous and ordered states.

Although the BF₂dbmOR luminophores in this series are identical throughout, with dipolar, H-bonding and arene stacking interactions likely,²⁶ even still, the alkyl chain substituents influence solid-state emission in measurable ways. For the shortest chain analogues, the addition of a single -CH₂- can have a dramatic effect on emission properties. As the chain length increases, the hydrocarbon not only serves as a spacer, decreasing dye-dye interactions, it can also induce self-assembly and promote order, however, this effect tapers off at C12, above which emission maxima show little change. Previous studies with BF₂dbmPLA polymer systems show blue shifted emission with increasing dye dilution reaching monomer emission for high molecular weight (20 kDa).³⁸ This was attributed to decreasing dye-dye interactions in high molecular weight materials. This is similar to known solvatochromic effects for difluoroboron β -diketonate dyes,¹⁷ but induced by dye concentration, not the solid state polylactide solvent. A similar trend is observed for Cn dyes as powders and C3-C18 films formed by slow evaporation, where a blue shift is expected upon dye dilution and in a non-polar hydrocarbon environment. However, the C18 substituent is considerably shorter than the shortest PLA chain and interactions of polar dyes in the Cn series are considerably stronger given closer dye-dye distances. Ordered assembly and aggregate emission are dominant factors for the Cn dyes compared to the amorphous polymers.

Mechanochromic luminescence

The mechanochromic luminescence behaviors of the dyes were also investigated. Powders were applied to quartz cuvette

surfaces with a cotton swab and then the thin transparent coatings were thermally annealed. Starting spectra of the TA samples were recorded, then the thin coatings were smeared and monitored over time by luminescence spectroscopy. Compared to TA samples, shearing red-shifted and broadened the emission and much longer lifetimes with multiexponential decays were observed for all Cn dyes but C1 (Table 2). As previously reported.^{27,36} luminescence properties of sheared samples were similar to UA spin cast films (differing by only 1-12 nm), suggesting that mechanical perturbation also produces amorphous states. Lifetime measurements also support this: comparable lifetimes are obtained for **CnUA** spin-cast films and smeared powders (τ_{pw0} range = 1-10 ns). Surprisingly, smeared C2 displayed significant differences compared with its spin-cast film counterpart. For example, even though there is little detectable difference between C2UA and C2TA spin-cast films in emission and solid-state morphology (Fig. 2a and 3), nonetheless when blue emitting $(\sim 475 \text{ nm})$, thermally annealed C2 samples were smeared, they displayed orange ML. Lifetimes also increased with smearing (τ_{pw0} TA: 6 ns, smeared: 19 ns).

The crystallinity of TA and smeared samples was investigated by XRD for C2, C6, C12 and C18 (Fig. 4, blue and red lines). Spectra showed that crystallization occurs upon heat treatment and mechanical perturbation leads to amorphous states. Crystallinities were indicated by the small sharp peaks on the heat treated sample spectra. Upon annealing, small peaks emerged at $\sim 6^{\circ}$ and 24° for C12, $\sim 8^{\circ}$ and 24° for C6, and a very small peak at 24° for C18 (Fig. 4), similar to XRD spectra for powder samples. Even though ML is observed for C2, there are no noticeable changes in the XRD spectra under these conditions.

Differential scanning calorimetry of powders revealed distinct melting and crystallization events upon heating and cooling (Fig. S4†). On the first heating cycle, the T_m endotherm is typically broader, and in many cases, a second, weaker, lower temperature endothermic feature is also evident, suggesting structural complexity in the "as isolated" powder. After thermal conditioning, on the second and subsequent heating cycles, peaks sharpen and the lower temperature feature typically disappears.

For 5 °C min⁻¹ scan rates, only T_m and T_c are observed (Table S4[†]). However, a slower scan rate (1 °C min⁻¹) for **C18** shows two additional weak features at ~86 °C and ~98 °C, possibly glass transitions (Fig. S5[†]).

Table 2Mechanochromic luminescence properties of Cn powdersapplied to quartz substrates

	$\mathrm{TA}^{a}\lambda_{\mathrm{em}}{}^{b}(\tau_{\mathrm{pw0}}{}^{c})$	Smeared ^{<i>a</i>} $\lambda_{em}^{\ \ b}$ ($\tau_{pw0}^{\ \ c}$)
C1	544 (30.61)	544 (31.53)
C2	472 (6.04)	509 (18.70)
C3	488 (9.12)	527 (12.46)
C5	491 (10.14)	514 (21.62)
C6	475 (5.24)	494 (13.17)
C12	459 (7.10)	496 (23.94)
C14	461 (5.80)	501 (19.95)
C16	470 (4.13)	508 (19.94)
C18	472 (3.12)	506 (23.04)

^{*a*} TA = thermally annealed. ^{*b*} Units are given in nm. ^{*c*} Pre-exponential weighted lifetimes.³⁰



Fig. 4 XRD spectra of powder (green), thermally annealed (TA) (blue), and smeared samples (red) for C2, C6, C12, and C18.

Another interesting qualitative observation is that the force required to elicit an optical response also varies across the series. For example, longer alkyloxy chain analogues (*e.g.* **C18**) required greater pressure for an observable color change, whereas for shorter analogues (**C3**), even slight pressure suffices. More systematic studies to quantify these force-induced effects will serve as the subject of future reports.

A unique feature of these boron dyes is their ability to spontaneously revert to the ordered emissive state after shearing at room temperature. Recovery times of \sim 3 hours for thin films of **C12** on glass²⁷ and \sim 1 day for BF₂AVB²⁶ on quartz were observed by fluorescence spectroscopy. Note that visually, the marks disappear even sooner than this on weighing paper substrates and that effects are thickness dependent. Because longer alkyl chains are capable of assembly, it is also interesting to test for chain length effects on spontaneous ML recovery processes (Fig. 5). Recovery time studies for **Cn** dyes were performed by applying samples (\sim 2 to 3 mg) to the surface of a quartz cuvette. The resulting films were thermally annealed to generate a starting ordered state and spectra were recorded. Then the TA samples were smeared, and their recovery was monitored over time at room temperature.

Blue emitting thermally annealed C2 films (475 nm) turned orange (\sim 510 nm) upon shearing, taking \sim 18 h to spontaneously recover to the stable TA state (\sim 475 nm). (Upon visual inspection the dye appears to recover in <30 min.) The blue fluorescent TA dyes C3 and C5 displayed quite similar behavior to C2, becoming orange upon smearing, then spontaneously blueshifting back to the stable TA form, with C3 recovering faster than C5 (25 min and \sim 1 day, respectively). Smearing C6 and C12 also turned the emission orange, which was noted visually, but these samples immediately recovered to green emission, and then gradually further blue-shifted. But after 9 days, the C6 emission stopped changing before full recovery to the original ordered TA state, as monitored by fluorescence spectroscopy. In contrast, C18 did not self-heal to green immediately and between 9 and 18 days, the emission had stabilized, suggesting that a full room



Fig. 5 Emission spectra for C2, C3, C5, C6, C12, C18 sheared powder films on quartz substrates monitored over time after smearing ($\lambda_{ex} = 365$ nm) (TA = thermally annealed, S = immediately after smearing, m = minutes, h = hours, d = days).

temperature recovery may not be possible. However, heating this smeared sample did produce the original state TA, which is how samples are fabricated originally, for testing. For C3–C18, a consistent trend was observed; longer alkyl chain length correlates with the increasing recovery time. On the other hand, C2 recovers much more slowly than C3. As observed for C2 throughout this study, ML behaviors too, are very different than the other dyes in the series.

Conclusions

In summary, the solid state and mechanochromic luminescence properties of BF₂dbmOR with different alkoxyl chain lengths were investigated. Crystalline powders, slow evaporated films and thermally annealed spin-cast film emissions displayed narrow, hypsochromic-shifted peaks and shorter lifetimes compared to the more amorphous unannealed films. Chain length dependent emission was observed for C3-C18 in both powders and slow evaporated films. Furthermore, solid-state fluorescence spectroscopy studies suggested that shorter alkyl chain lengths affect the optical properties more significantly than longer alkyl chain length (n > 12). This is exemplified by spin-cast C2, C3UA and C5TA films that differ by few carbons but all exhibit unique behaviors. All Cn dyes but C1 are mechanochromic luminescent, showing bathochromic shifts, and broad, structureless bands upon smearing. In addition, lifetime measurements revealed longer decays for smeared powders, suggesting that excimer emission is activated upon smearing. Spontaneous recovery times on quartz surfaces generally increase with longer alkyl chains, but **C2** is an exception to this trend. Interestingly, when the alkoxyl chains surpass a certain threshold, which appeared to be n = 6 in this study, the smeared powders did not revert to the ordered TA states under the reported experimental conditions and on quartz substrates. Additional structure-property studies, further characterization and quantification of force induced effects, and mechanosensor applications serve as topics for future work.

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